

Coupled Biogeochemical Processes in the Soil and Soil-Plant Systems Responsible for Enhanced Transport of Plutonium in the Vadose Zone

Fred J. Molz¹, Deniz I. Demirkanli¹ and Daniel I. Kaplan²

¹Clemson University

²Savannah River National Laboratory

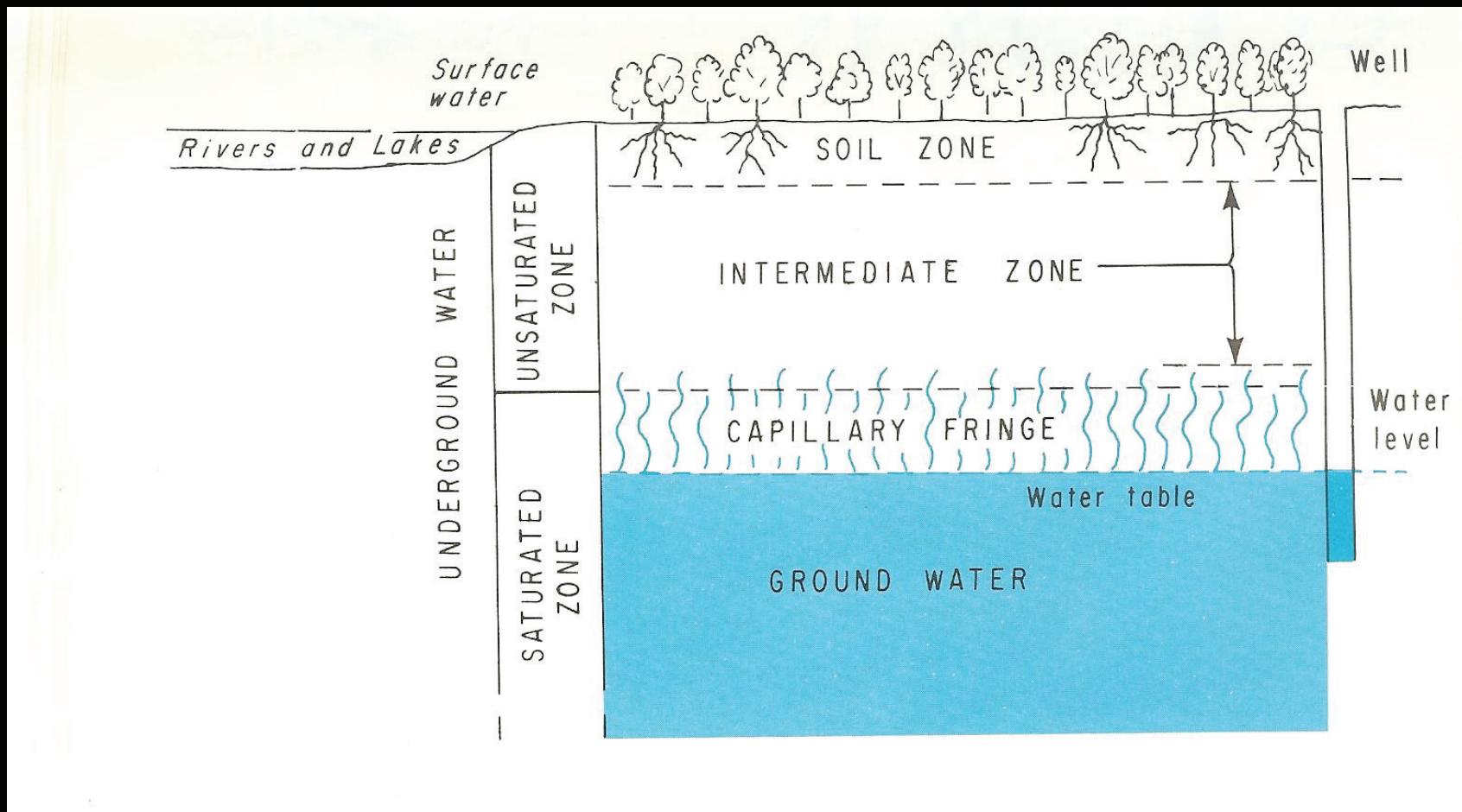
2008 DOE ERSP Principal Investigator (PI) Meeting
Lansdowne, Virginia

April 7 - 10, 2008

Outline

- SRNL Lysimeter Experiments:
 - Location, Climate, Results.
- Pu Reactive Transport Model Development with:
 - Transient Flow in Soil with Root Water Uptake.
 - Comparison with Experiments.
 - Root Water Uptake and Pu Transport in the Root/Stem Xylem Coupled to Flow and Transport in the Soil.
 - Comparison with Experiments.
- Conclusions

The vadose zone extends from the water table to the land surface. It contains several sub-zones, and the hydrology is highly dynamic with many interdependent (coupled) processes. In vegetated soils, plant roots play an important role, along with microbes.



SRS Lysimeter Experiments

- Initiated: 1980s (11/25/1980)
- Purpose: To evaluate long-term Pu migration

33.0 cm
Surface

21.6 cm

Pu Source 51.0 cm

Sediment



Screen
Collection Reservoir



Pu Source in the Experiment	Field Duration (yr)	Storage Duration (yr)	Initial Activity (μCi)
$\text{Pu(IV)}(\text{NO}_3)_4$	~11	~10	527
$\text{Pu(IV)}(\text{C}_2\text{O}_4)_2$	~11	~10	518
$\text{Pu(III)}\text{Cl}_3$	~11	~12.4	585

- Pu activity concentration distributions are measured along a core.

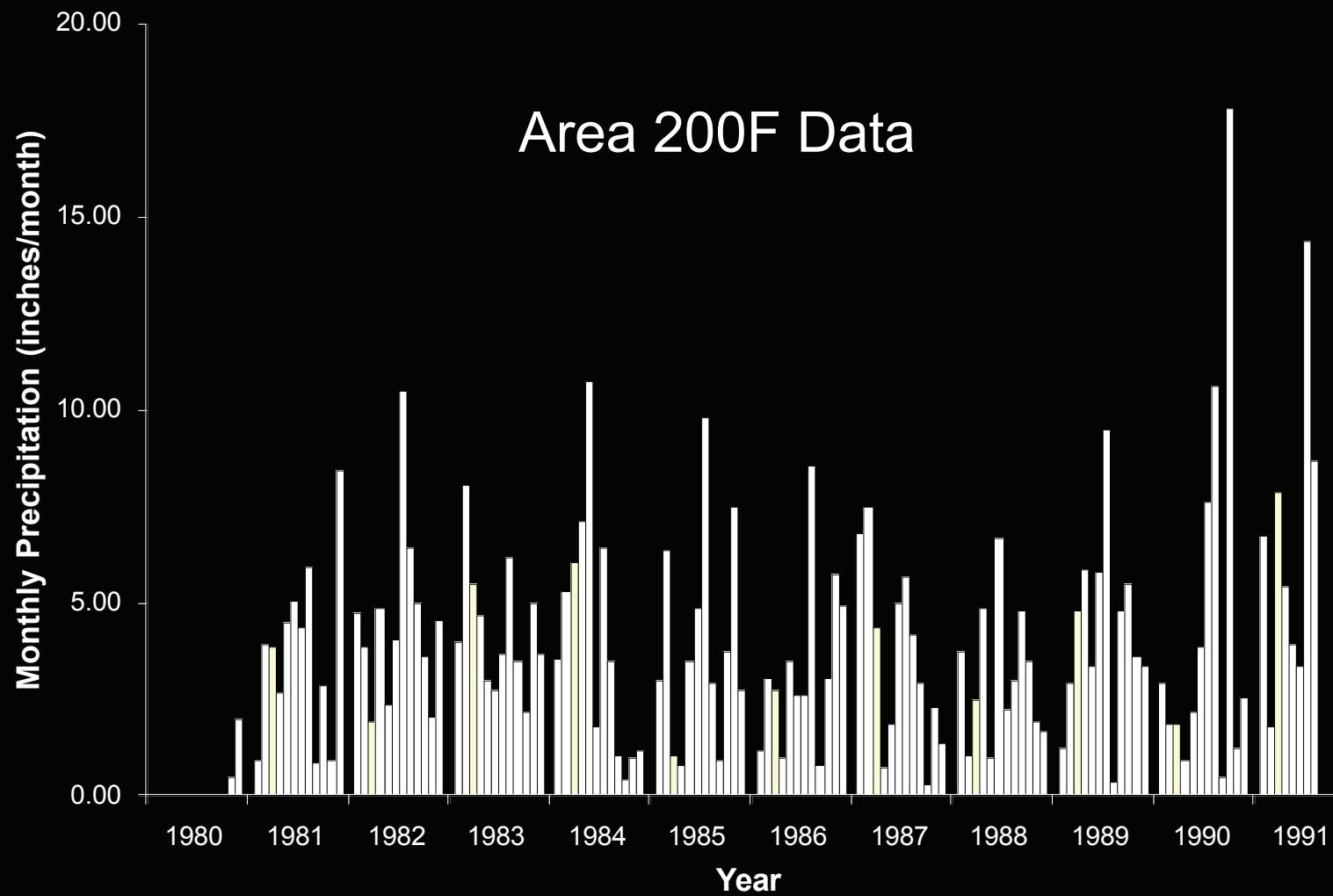
Demirkanli et al. 2007, 2008; Kaplan et al., 2004; 2006; 2008

Lysimeter Experiments – Field Conditions

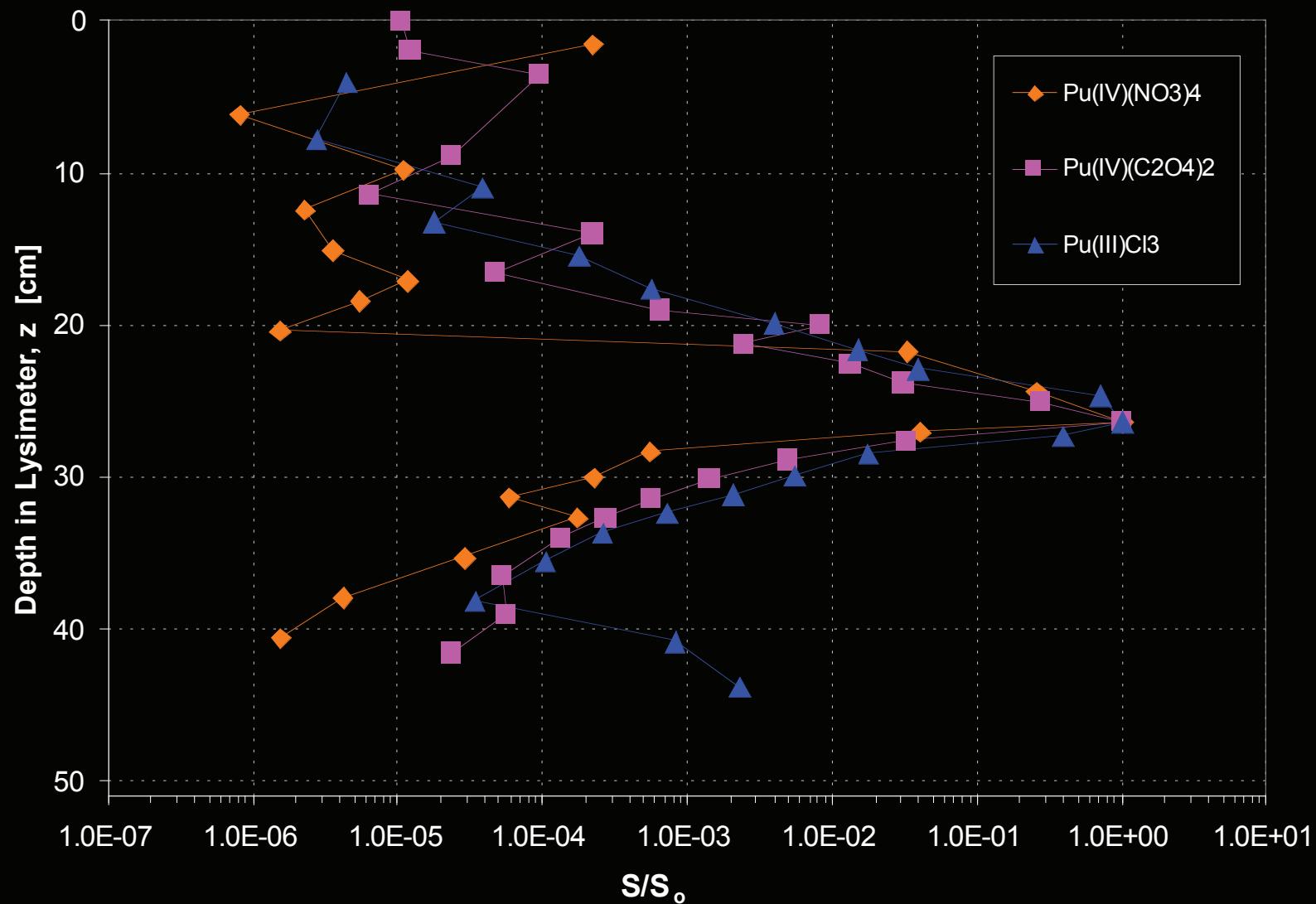


Lysimeter Experiments – Rainfall Data

- Rainfall data were collected at the SRS and combined with climatological data and lysimeter leachate volume data. The resulting water balance yielded the daily evapotranspiration.



Measured Pu Distributions with Reduced Sources. (Superimposed by source location.)



The mathematical model used to simulate the measured Pu activity distributions is based on the following concepts

- Rainfall (measured) enters the lysimeters as infiltration.
- Pu transport in the soil is controlled by advection, dispersion and sorption, with advection and sorption dominating.
 - Two forms of Pu are assumed, oxidized Pu (Pu_{o} – high mobility) and reduced Pu (Pu_{r} – low mobility). Pu_{r} is the dominant form.
- A surface-catalyzed redox reaction takes place wherein $Pu_{\text{o}} \leftrightarrow Pu_{\text{r}}$.
 - The reaction kinetics are assumed to be proportional to the sorbed activities (1st order). Rate constants are used as fitting parameters.
- Water is removed from the soil by evapotranspiration (ET), with transpiration dominating.
 - ET is calculated as the difference between rainfall (measured) and lysimeter drainage (measured).
 - Transpiration is distributed vertically in proportion to the rooting density (Measured on post-experiment soil cores).

(What are the implications of the measured rainfall, drainage, ET, rooting density and Pu activity distributions)?

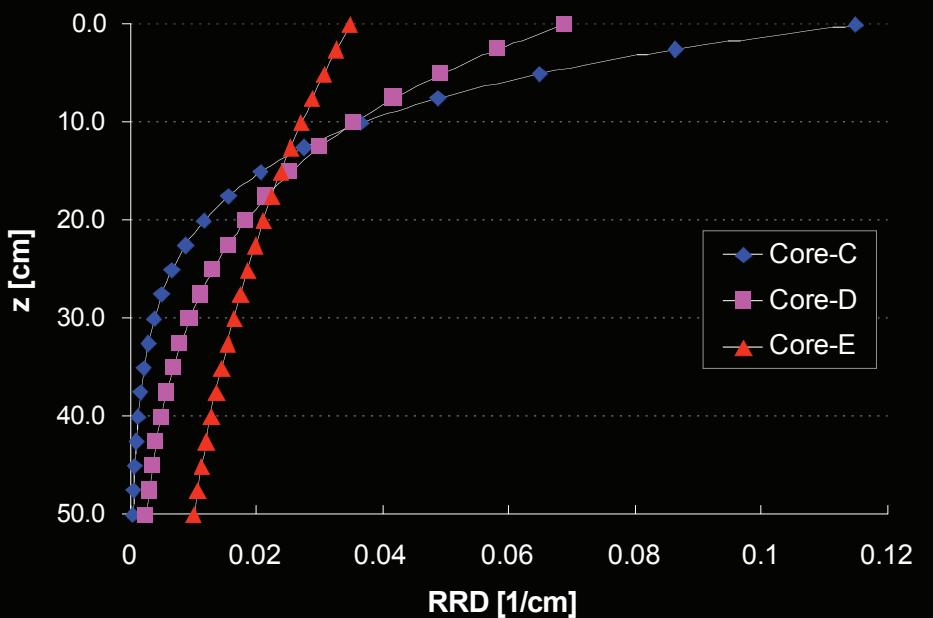
Variably Saturated Flow Model

Governing Equation:

- One-dimensional, pressure-head based, mixed-form of variably saturated flow equation (VSFE):

$S(z, \psi)$ = Root water uptake function due to transpiration.

($RRD(z)$ = relative root density.)



THROUGH SOIL TRANSPORT EQUATIONS

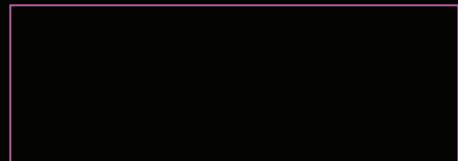
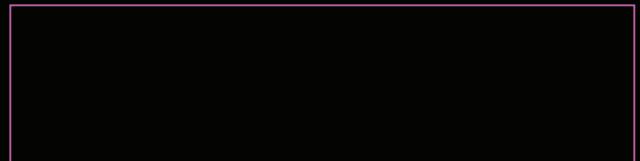
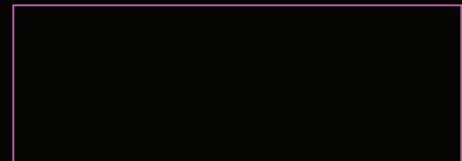
Mass (Activity) Balance:

Puo: Oxidized Pu

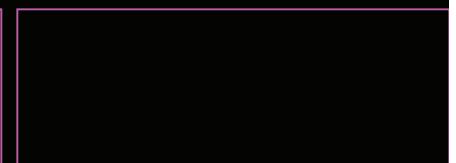
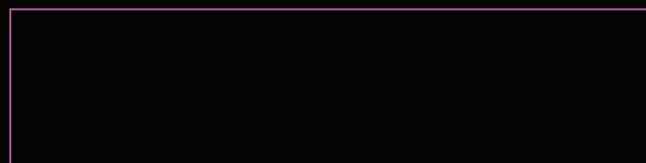
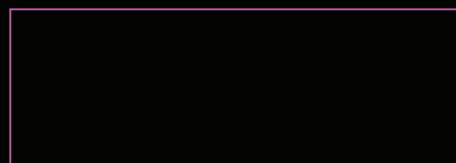
(transp. terms)

(reaction terms)

(source term)



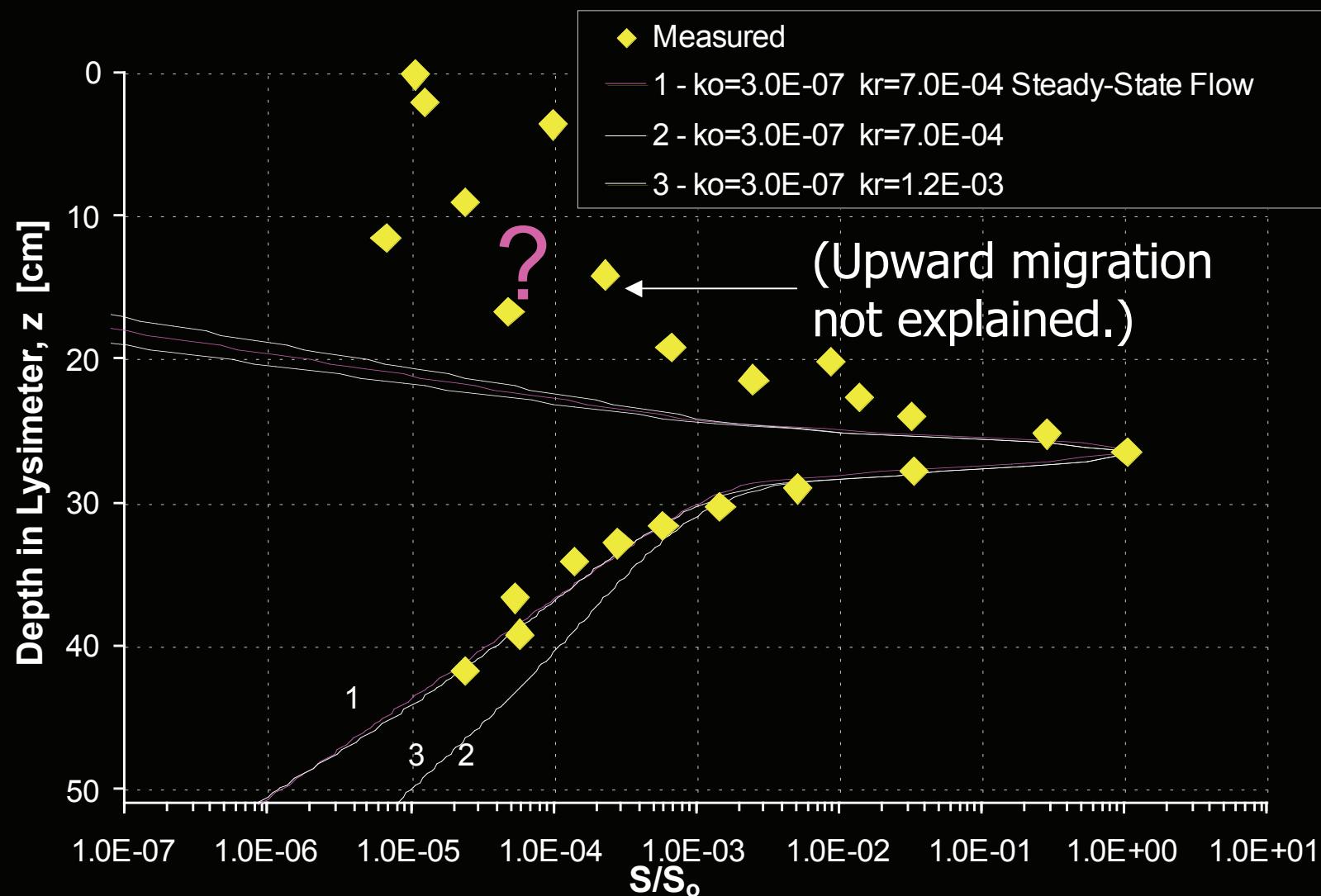
Pur: Reduced Pu



What processes do these equations couple?

- The main flow and transport driver is infiltration caused by rainfall (input to the variably saturated flow equation (VSFE)).
 - Required soil hydraulic properties are based on measured particle-size distributions, implied van Genuchten functions and a few unsaturated hydraulic conductivity measurements on soil without roots.
- A sink term in the VSFE couples soil water flow to transpiration and root distribution. Solving the VSFE yields the soil water velocity field, represented by $v(z,t)$ and the water content field $\theta(z,t)$.
- $v(z,t)$ and $\theta(z,t)$ are the coupling processes between reduced source Pu transport (Pur) and soil water flow (first transport equation).
- Surface-mediated redox reactions couple Pur transport to oxidized Pu transport (Puo). Once created, Puo transport is also coupled to soil water flow by $v(z,t)$ and $\theta(z,t)$ (second transport equation).

Model Results: Variably Saturated Flow Pu(IV)(C₂O₄)₂

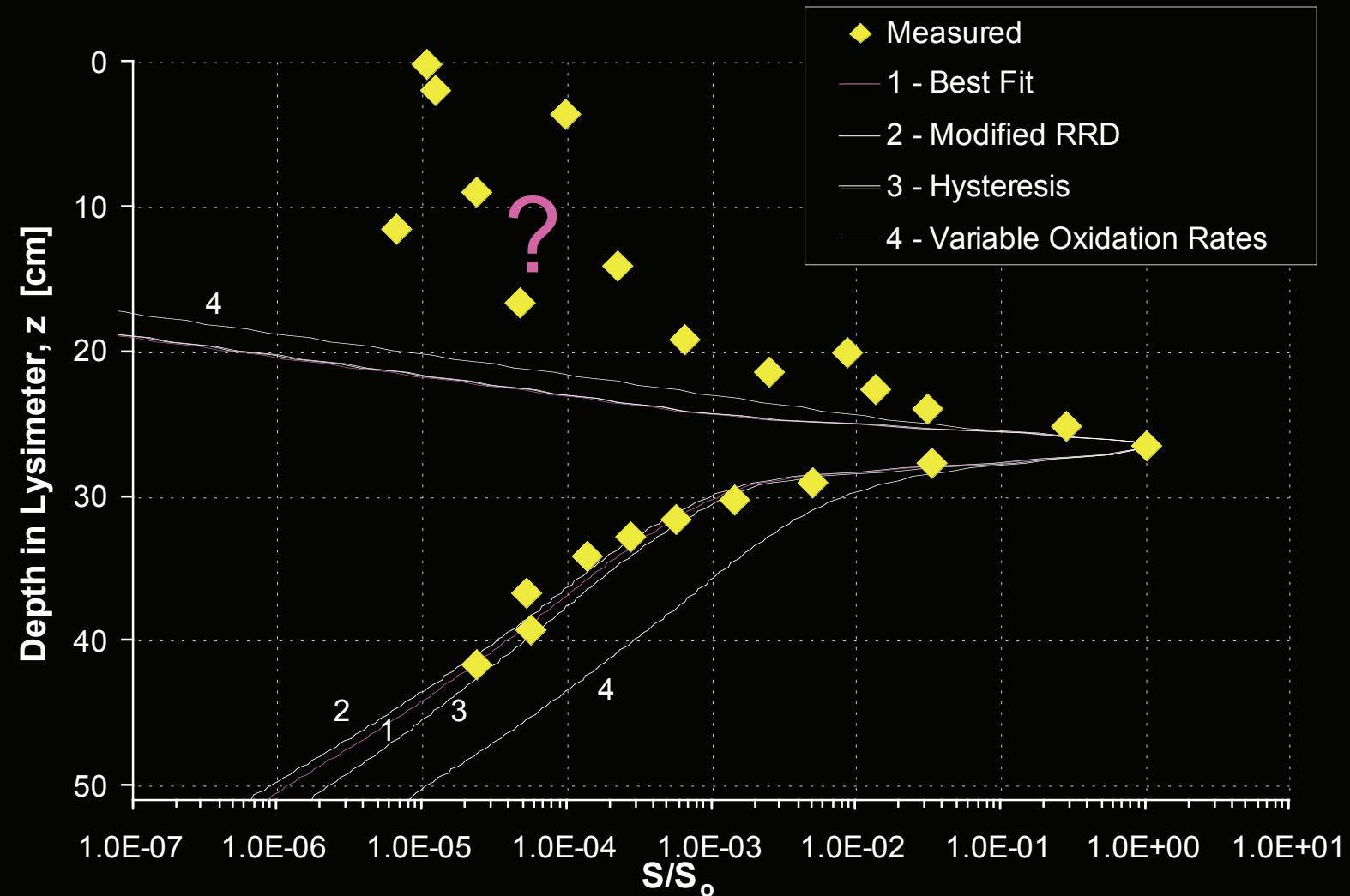


[Retardation factors = 15 (PuO) and 10.000 (Pur)]

Study of Possible Soil-Based Mechanisms to Explain Upward Migration

- 1) Use of a modified root distribution to maximize upward flow.
- 2) Inclusion of hysteresis, which maximizes hydraulic conductivity when water content is falling.
- 3) Making the reaction rate constants air-content-dependent, so that relatively more oxidized Pu (most mobile form) is produced under drying conditions when water flow is upward.

Model Results: Variably Saturated Flow (Pu(IV)(C₂O₄)₂)



(Tentative Conclusion: Pu, not just water, must be moving upward in plant roots.)

Root Xylem Transport Model: Transient Flow with Root Pu Uptake

- To further investigate the upward Pu migration:
 - Root Pu transport equations are developed and coupled to the in-soil transport equations and the variably saturated flow equation through a root solution uptake (source) term.
- The source terms driving the xylem transport are:
 E (Uptake Efficiency) varies between 0 and 1.

Governing Equations for the Root System

Pur:

(z-dependent adv./disp. Terms)



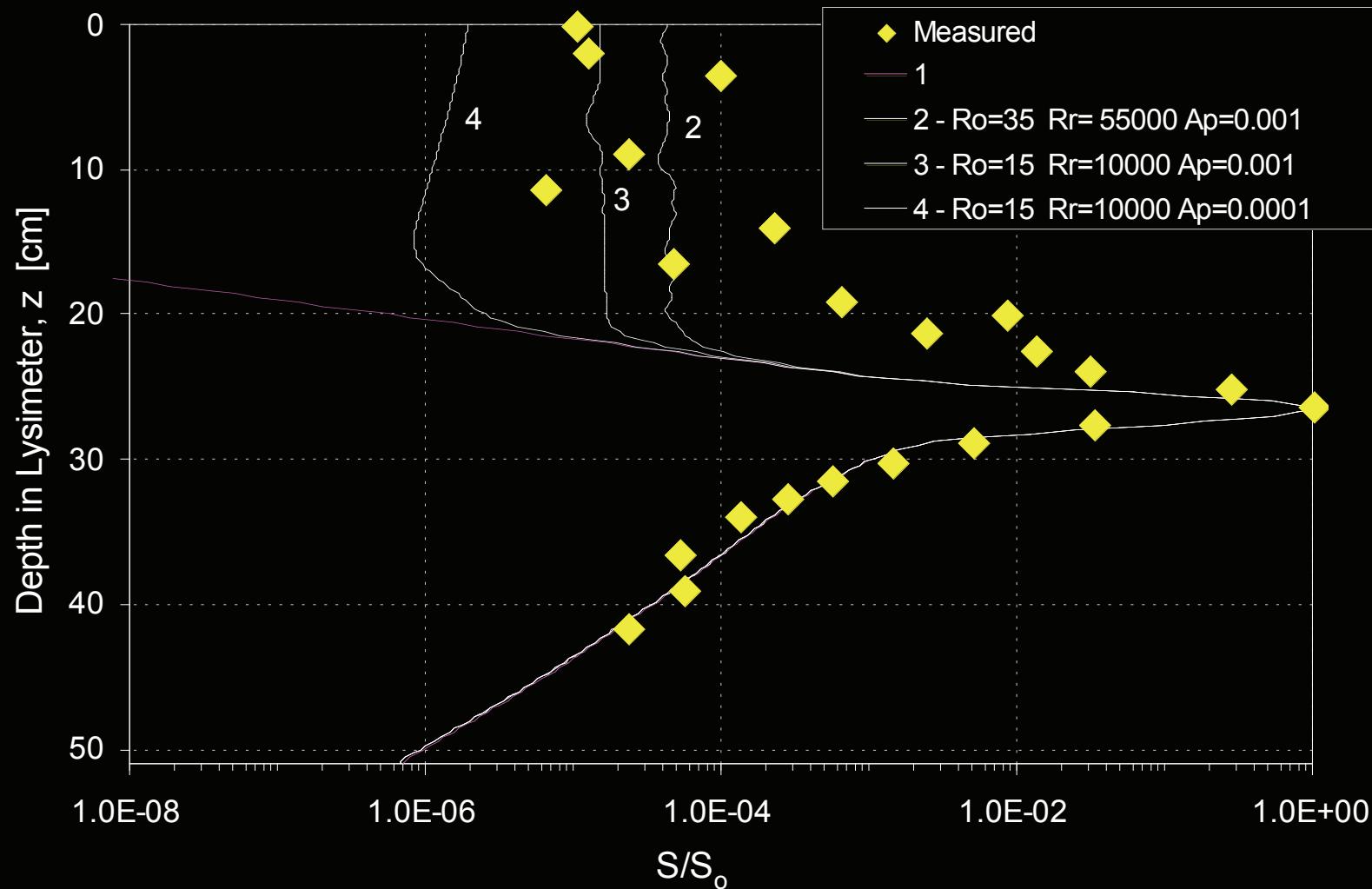
Puo:



Model Parameters

Model Results: Variably Saturated Flow and Root Pu Uptake/Translocation

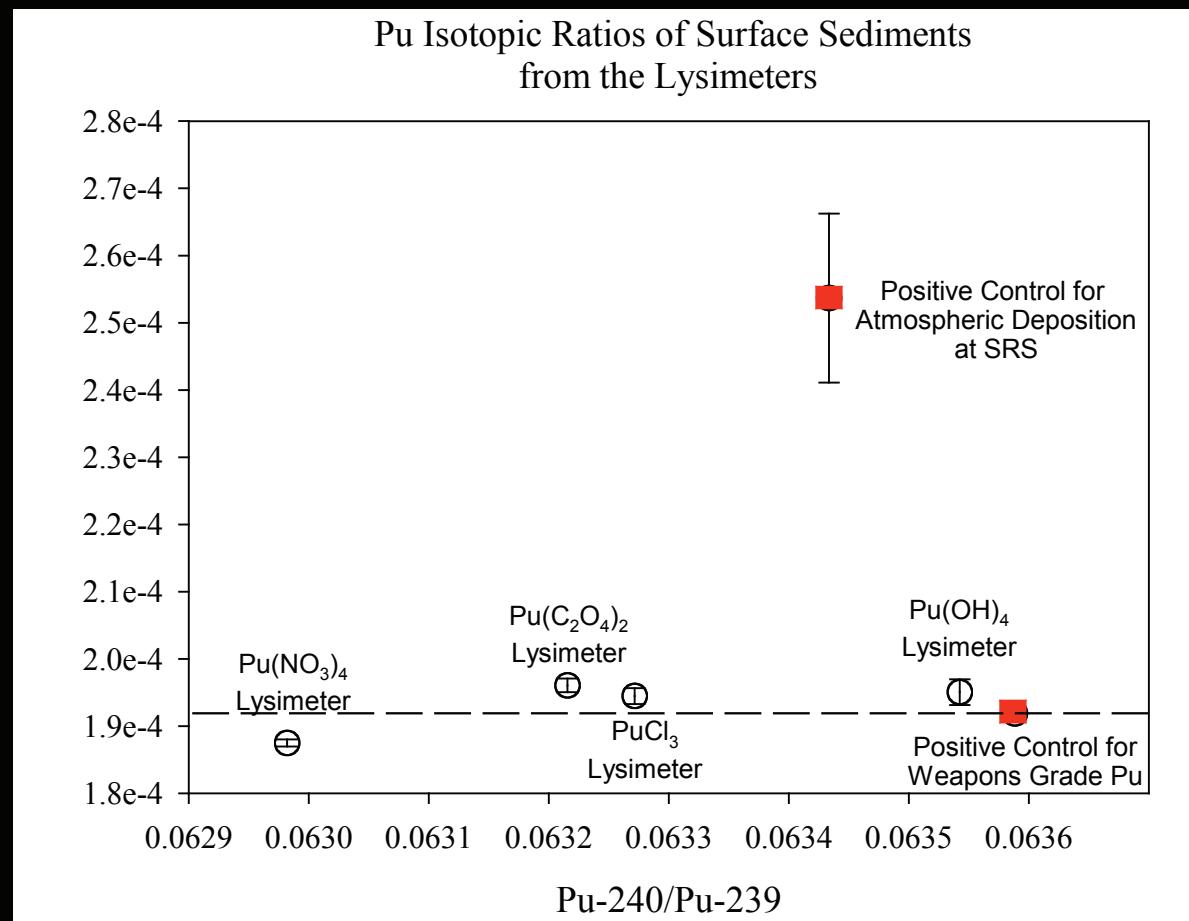
$\text{Pu(IV)}(\text{C}_2\text{O}_4)_2$



What did root xylem flow and transport models tell us?

- Under hot, moist, drying conditions, upward water velocities in plant xylem can be thousands of times faster than upward velocities through soil.
- This provides an upward pathway for reduced Pu transport even though it is likely highly retarded.
- The model suggests that some reduced Pu and virtually all oxidized Pu will be swept out of the root xylem and into the above-ground xylem.
- Since the above-ground plant parts will die back each year and decay on the surface, a Pu activity surface residue should build up.
- When this prediction was reported to the SRNL, it was found that such a reside was originally detected, but assumed to be due to atmospheric fallout, similar to that found at other SRNL locations.

Using thermal ionization mass spectroscopy (TIMS), it was verified that the Pu detected in the lysimeter surface residue came from the buried source, not atmospheric fallout.



Tentative Conclusions

- Hysteresis, modified root distribution functions, and air-content dependent oxidation rate constants were not able to explain the observed upward migration characteristics of Pu.
- Small amounts of Pu uptake by plant roots and translocation in the transpiration stream creates a realistic mechanism for upward Pu migration, and it is also consistent with the previously simulated downward movement.
- Realistic xylem cross-sectional areas, root density and transpiration rates imply high flow velocities under hot, moist conditions.
- Such flow velocities produce the correct shape for the observed activity distributions in the top 20 cm of the lysimeter soil.
- Simulations imply that Pu should have moved into the above-ground grass tissue during the duration of the experiments. Measured Pu-242/239 isotope ratios show that surface activity residues come from the buried sources.

Suggested Future Research

- The proposed surface-mediated redox model may not be entirely correct. (Right for the wrong reason?). We are now simulating the results of other possible chemical reaction conceptual models to determine if they are compatible with the lysimeter data.
- The measured activity distribution just above the source is not simulated well. We may be missing a phenomenon such as enhanced Pu mobility due to root and/or microbial activity. This possibility is also being studied.
- Even though some interesting predictions resulted, we are not using our simulation models in a classical predictive sense. We are using them to explore the implications of the measurements (rainfall, lysimeter drainage, ET, root density, soil particle size distribution, Pu activity distributions) that were made. This is more like “computer-aided thinking”.
- This procedure is suggesting many future measurements that would be beneficial to perform.

Acknowledgements

- Brian A. Powell (formally LLNL, now Clemson University)
- Steven M. Serkiz (SRNL)

Funding:

- Support from U.S. Department of Energy (Contract # DE-FG02-07ER64401) and the Savannah River National Laboratory are acknowledged gratefully.
- Partial PI salary support from Clemson University and the State of South Carolina is also acknowledged gratefully.

Questions?